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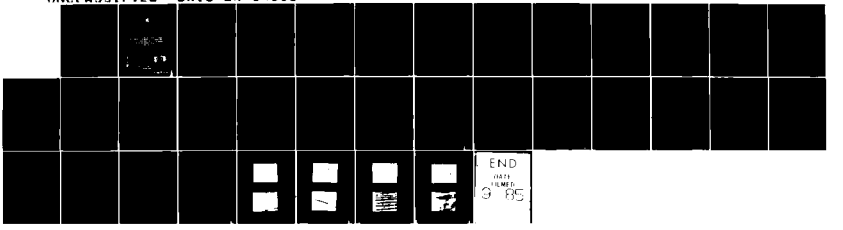

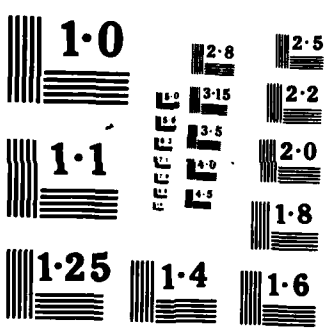
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EFFECT OF CARBON FIBRE SURFACE TREATMENT ON MOISTURE ABSORPTION AND INTERLAMINAR SHEAR STRENGTH OF CARBON FIBRE/EPOXY RESIN COMPOSITES

by

Om K. Joshi

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SUMMARY

Carbon fibres surface treated to eight different levels of the standard treatment were moulded into unidirectional composites in an epoxy resin. The composites were immersed in boiling water or exposed to a hot humid environment (70°C, 95% RH), and the water absorption, swelling and interlaminar shear strength were measured. The reversibility of these effects was studied initially by drying the composites at 70°C in a vacuum oven and further by repeated hygrothermal cycling. In general more moisture was absorbed for the lower levels of surface treatment where the bond between the fibre and matrix was weaker. Studies of reversibility showed that there was a greater probability of permanent damage for low fibre matrix bond strengths and for specimens immersed in boiling water.

Departmental Reference: Materials/Structures 83

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1 INTRODUCTION

The interlaminar shear strength (ILSS) of a carbon fibre composite is dependent on the transfer of the stress between the fibres and the matrix and upon a strong interfacial bond that resists failure. This is converse to the role played by a preferential failure of the interfacial bond to increase the toughness of a composite. The bond between the fibres and the matrix depends on the type of epoxy resin used and on the surface treatment of the carbon fibres[1]. Thus for any given epoxy resin, as the surface treatment of the fibres is increased the mechanical properties controlled by the strength of the interface bond, *ie* shear and compression would increase to give an optimum value.

This optimum value was defined for the (high strength), HT fibres as the standard or 100% fibre surface treatment. As the (high modulus) XA fibre replaced the HT fibres, the fibre surface treatment was not altered. Recent studies have shown brittle failures and low notched tensile strength of unidirectional and cross ply composites[2]. This was attributed to an excessively strong interfacial bond. Compression strengths of uni- and multi-directional CFRP increased with increasing fibre surface treatment up to 10% after which no improvement in strength was obtained[3]. It was therefore valid to evaluate the variation of the ILSS with the fibre surface treatment.

It is generally known that the presence of moisture in a CFRP laminate decreases its ILSS by plasticizing the resin and by degrading the fibre-matrix bond. Previous work on CFRP with 100% fibre surface treatment showed that this decrease in ILSS was dependent only on the moisture content and not on the method of exposure[4]. Hence two modes of exposure; immersion in boiling water and exposure to 95% RH at 70°C were evaluated.

The effects of moisture are thought to be reversible. Hence on drying a 'wet' composite, the ILSS should be recovered. This is however not always the case. Hygrothermal cycling could cause further damage to the matrix and the interfacial bond.

In the work now reported the effect of moisture on the ILSS during hygrothermal cycling of a CFRP was studied for eight composites made from the same batch of resin. The fibres had different surface treatments between 0% and 100% of the standard treatment. Dimensional changes during hygrothermal cycling were measured. The variation in the interlaminar shear strength is explained in terms of the adhesion of the resin to the fibres, microcracking in the resin, plasticization and lowering of the glass transition temperature of the resin, and the 'physical ageing' of the resin due to the available 'free volume' as the composite cools from its curing temperature.

2 EXPERIMENTAL DETAILS

Courtauld's Grafil XA carbon fibres were subjected to various levels of surface treatment, expressed as a percentage of the standard surface treatment;

Batch A with 0%, 1%, 2%, 5%, 10%, 25%, and
Batch B with 25% and 100% surface treatments.

These fibres were pre-impregnated in Ciba Geigy's BSL 914 epoxy resin. Unidirectional laminates, 2 mm thick were moulded in an autoclave to a nominal fibre volume fraction of 60%. Each of the laminates was cut into test pieces (20 mm × 12.5 mm).

Five samples from each laminate were dried in a vacuum oven at 70°C to assess the amount of moisture already present in the laminates.

Fifteen 'as-received' samples were immersed in boiling water for 1 week and fifteen were exposed to a temperature of 70°C and a relative humidity of 95% until an equilibrium weight was recorded (approximately 2570 hours). Five specimens from each 'exposed' set were tested for interlaminar shear strength in three point bending[4]. The remaining ten exposed samples from each set were dried at 70°C in a vacuum oven until a weight loss of less than 0.01% in 24 hours was achieved. Five specimens of each set were tested in three point bending and the other five were tested after re-exposure to the original hot-wet environment to attain the equilibrium moisture content.

The change in weight, length, width and thickness of the specimens was monitored during each exposure. The total moisture contents of specimens was calculated by adding the increase in weights of 'as-received' specimens, during the exposure to hot-wet condition, to the weight lost by the 'as-received' specimens when dried at 70°C in a vacuum oven. This procedure was adopted rather than drying the specimens prior to exposure because such pre-drying can alter the absorption characteristics of carbon fibre composites[5]. Similarly the change in the dimensions was calculated using the dried state as datum.

The interlaminar shear strength of the specimens tested in the short beam three-point bend mode was calculated from their failure stress values as described elsewhere[6].

The ILSS test piece fracture surfaces were studied using the optical and scanning electron microscope.

3 RESULTS

3.1 Moisture absorption

The amount of moisture present in the 'as-received' specimens is plotted (Fig 1); as the weight during drying against the percentage fibre surface treatment. Batch 1 laminates contained between 0.35 and 0.47 weight per cent moisture whereas in batch 2 laminates there was between 0.45 and 0.51 weight per cent moisture present. The amount seemed to be independent of the fibre surface treatment.

When the specimens were immersed in boiling water for 1 week (Fig 2), composites made from fibres with 0% and 1% surface treatment absorbed significantly more moisture (3.6 weight per cent) than those made from fibres with higher surface treatments (see Fig 2). There was no significant difference in the amount of moisture absorbed by composites made from fibres with surface treatment between 2% and 100% (approximately 2.2 weight per cent).

The specimens which were exposed to 70°C and 95% relative humidity (RH) showed a gradual decrease in equilibrium moisture content as the fibre surface treatment increased from 0% to 25% (1.82 to 1.45 weight per cent). There was no significant difference in the amounts of moisture absorbed by the composites made from fibres with surface treatments of 25% and 100%.

In both the immersion and the hot-wet exposure experiments, batch 2 samples absorbed slightly more moisture than batch 1 specimens. The difference was greater in the aged samples where the batch 1 composite with fibre surface treatment of 25% absorbed 1.45 weight per cent moisture and the batch 2 composite with a similar fibre surface treatment absorbed 1.75 weight per cent moisture.

The saturated moisture absorption was greater for the boiled samples for all levels of fibre surface treatments. The difference was greatest at 0% fibre surface treatment, where the boiled samples absorbed twice as much moisture as the aged samples (3.62% compared with 1.82%). For composites with fibre surface treatment greater than 5%, the difference in the maximum amounts of moisture absorbed between the boiled samples and the aged samples was approximately 0.5 weight per cent.

3.2 Hygrothermal cycling

Hygrothermal cycling was carried out for specimens which had been immersed in boiling water and for specimens that were exposed to 70°C and 95% RH.

The specimens immersed in boiling water for 168 hours and then dried in a vacuum oven at 70°C, retained approximately 0.5% by weight moisture, except for specimens from the composites with 0% and 10% fibre surface treatment (see Fig 3). The specimens with 10% fibre surface treatment showed a large scatter in the dimensional and mechanical properties. The retention of moisture in both the batch 1 and batch 2 composites was similar. As the dried samples were immersed in boiling water again, the composites made from fibres with surface treatments below 5% absorbed more moisture (approximately 0.4 to 0.5%) than they had during the first boil. At the higher fibre surface treatments the absorption of moisture after the second boil was similar to that after the first boil.

As the samples exposed to 70°C and 95% RH were dried, the composites with fibre surface treatment of 0% from batch 1 and 100% from batch 2 retained approximately 0.25% by weight of moisture whereas the rest of the composites retained about 0.45% by weight moisture (see Fig 4). When these dried samples were re-exposed to 70°C and 95% RH, they all absorbed more moisture than during the first exposure. The specimens showed a slight increase in moisture absorption as the fibre surface treatment increased. This trend was opposite to the initial ageing where the moisture absorption decreased as the surface treatment was increased.

Comparing the results obtained after the specimens had been immersed in boiling water with those obtained after exposure to 70°C, 95% RH; the amount of moisture retained after drying the wet samples was similar. The moisture content after the second exposure to 70°C and 95% RH was similar to that of specimens that had been immersed in boiling water for 1 week, and also to the pre-dried specimens exposed to 70°C, 95% RH.

3.3 Dimensional changes

The changes in length (parallel to the fibre direction), width and thickness (both transverse to the fibres) were monitored throughout the programme. The changes in volume

when the specimens were exposed to the hot-wet conditions, dried at 70°C in a vacuum oven and re-exposed to the initial hot-wet environment were calculated.

The length of the specimens did not change significantly during the hygrothermal cycling. The data is given in Table 1. The length variation (if any) was independent of the fibre surface treatment of the composite.

The increase in the width of the specimens which had been immersed in water for 168 hours was approximately 1.3% for composites with fibre surface treatment less than 1% (see Fig 5). For the rest of the specimens, the increase was of the order of 1% and was independent of the fibre surface treatment. On drying these boiled samples, the composites with fibre surface treatment less than 1%, regained their original width whereas the rest of the samples (up to 100% fibre surface treatment) retained some swelling (of the order of 0.2%). As these dried samples were immersed in boiling water again, the width increased to give similar values to those after the first immersion.

The change in thickness of the specimens as they were immersed in boiling water was more marked than the change in length or the width for specimens with the lower fibre surface treatments (less than 2%; see Fig 6). The scatter in the values was also greater. The change in thickness decreased from about 3.5% to 1.7% as the fibre surface treatment was increased from 1% to 5%. There was no further effect as the fibre surface treatment was increased from 5% to 25% on the change in thickness. There was a slight hint of a decrease in the change in thickness for the specimens with 25% and 100% fibre surface treatment in batch 2.

As the boiled samples were dried at 70°C, the composites with fibre surface treatment less than 5% retained some swelling. This in thickness, decreased from 1.3% to 0.3% with an increase in the fibre surface treatment from 0% to 5%. As the fibre surface treatment was increased from 5% to 100%, the composite tended to return to its original thickness on drying. Batch 2 specimens retained some swelling (0.1 to 0.2%). As these dried samples were reboiled, the composites with carbon fibre surface treatments 0% and 1% returned to the same thickness as they had after the first boil. The specimens with fibre surface treatment of 2% showed a greater increase in thickness after the second boil whereas the effect was reversed for specimens with fibre surface treatments between 5% and 25% of batch 1 and batch 2 specimens. The composite with 100% fibre surface treatment (in batch 2) was thicker after the second boil than after the first boil (1.25% compared with 1.0%)

The change in volume of the unidirectional carbon fibre composite laminate with different levels of fibre surface treatment is shown in Fig 7. The change in volume was dominated by the change in the thickness of the composite but moderated by the lower changes in the width and the length of the composite. The results can be divided into two sets. For composites with fibre surface treatment below 2%, the changes in volume during the hygrothermal cycling are significantly higher than for specimens with fibre surface treatments above 2%. The scatter in the results was higher for composites made from fibres with lower surface treatments. As the composites were dried, the specimens with the fibre surface treatment below 2% did not regain their original volume whereas

more than 80% recovery was obtained for specimens with the higher fibre surface treatment. On reboiling, the specimens with 0% and 1% fibre surface treatment swelled to give a value similar to that obtained after the first boil. The specimens with 2% fibre surface treatment swelled more than they had after the first boil. Specimens with higher fibre surface treatments (5-25%) did not swell as much after the second boil as they had during the first boil. Batch 2 specimens showed no difference in the swelling after the first and the second immersion in boiling water.

When the carbon fibre composites were aged at 70°C and 95% RH for 15½ weeks, the length of the specimens did not alter significantly. The data are given in Table 2. The increase in the width was approximately 0.75% for all specimens regardless of the fibre surface treatment (see Fig 8). As the aged samples were dried at 70°C, the width of the specimens decreased to give a value below that of the original specimens. The minimum decrease was 0.5% below the original width for specimens with fibre surface treatment of 10% (batch 1) and 25% (batch 2). The decrease seemed to be independent of the fibre surface treatment. As the dried samples were re-aged at 70°C and 95% RH all the specimens swelled up to give widths similar to those obtained after the first exposure to this environment. The specimens with fibre surface treatment of 10% gave a lower value. A large variation in other results for these specimens was also observed, implying that the quality of the specimens may not have been consistent.

As the composites were aged, the increase in the thickness of the specimens (0.75%) was similar to the increase in their width (see Fig 9). However the standard deviation on the results was higher for the thickness measurements (the 10% fibre surface treated composite showed the maximum variation). The increase in thickness was independent of the fibre surface treatment. As the composites were dried, all the specimens became thinner than they had been originally. A slight decrease in the thickness was noted as the fibre surface treatment increased. Batch 2 specimens had thicknesses nearer the original value and the scatter was lower. As the dried specimens were re-aged at 70°C and 95% RH, the increase in the thickness of the composite with 0% and 100% fibre surface treatment was similar to that obtained after the first ageing. For the specimens with fibre surface treatments of 25% (batch 1 and batch 2) the increase in the thickness was less after the second ageing than after the first exposure by approximately 0.4%).

The increase in the thickness of batch 2 specimens with 100% fibre surface treatment after re-ageing was only slightly higher than that after the first exposure. In batch 1 specimens, a decrease in the change in thickness was observed as the fibre surface treatment was increased from 0% to 25%. The effect was reversed between specimens with fibre surface treatment 25% and 100%.

The increase in volume after the first exposure to 70°C and 95% RH was independent of the fibre surface treatment and varied between 1.25% and 1.7% (see Fig 10). The scatter in the results was large. As the aged samples were dried at 70°C, the volumes decreased to values less than those of the original samples dried at 70°C. There was considerable scatter in the results. Thus a decrease in volume between 0.25% and 1.0% below the original volumes was obtained. The specimens with the higher fibre

surface treatment (25% and 100%) did not shrink as much as the specimens with lower fibre surface treatments.

On re-ageing the dried specimens, the change in volume for the batch 1 specimens, up to 10% fibre surface treatment, was similar to the increase in volume after the first exposure. The specimens with fibre surface treatment 25% and 100% showed a smaller increase in volume after the re-ageing.

3.4 Interlaminar shear strength

The interlaminar shear strength of the composites made with fibres having varying amounts of surface treatment was evaluated after each cycle of hygrothermal ageing, *ie* after exposure to the hot-wet environment, after drying and then after re-exposure to the initial hot-wet conditions.

The 'as-received' specimens showed an increase in the interlaminar shear strength, ILSS, as the fibre surface treatment increased from 0% to 10%. There was no appreciable increase in ILSS up to 25% (batch 1) and 100% (batch 2) fibre surface treatment. The maximum strength measured for the as-received specimens was 98 MPa for the composite with 100% fibre surface treatment.

Drying the as-received specimens at 70°C in a vacuum oven did not affect the interlaminar shear strength of the composites for batch 1 material (see Fig 11). For the batch 2 material, the ILSS of 25% and 100% surface treated fibre specimens was similar in contrast to the as-received condition. The amount of moisture present in the as-received condition of the 100% fibre surface treated specimens was slightly greater. This may be enough to cause the ILSS to be greater as discussed in previous results[4].

On immersion in boiling water for 1 week, all eight composites showed a decrease in interlaminar shear strength, ILSS; the losses were greater for specimens with lower fibre surface treatments. The composite with 0% fibre surface treatment showed a decrease from 66 MPa to 22 MPa (a decrease of 67%) on boiling, whereas the composite with 25% fibre surface treatment decreased in strength from 91 MPa to 73 MPa (a decrease of 20%) when boiled.

When the boiled specimens were dried at 70°C the ILSS did not recover fully. The composite with 0% fibre surface treatment had a strength of 31 MPa (*cf* 66 MPa for the as-received samples) and the composite with fibre surface treatment greater than 25% had a strength of 85 MPa (*cf* 91 MPa for the as-received samples). The results were similar for the batch 2 samples.

On reboiling, the specimens showed strengths similar to those obtained after the first immersion in boiling water, implying that the maximum damage occurred during the first cycle.

When the 'as-received' specimens were exposed to 70°C and 95% RH and then tested, the ILSS decreased. The maximum decrease occurred for specimens containing fibres with no surface treatment where the strength dropped from 66 MPa to 47 MPa (a decrease of 29%) after exposure. For specimens with 25% fibre surface treatment, the decrease was from

91 MPa to 83 MPa (9%) and a similar decrease was observed for specimens with 100% fibre surface treatment.

As the 'aged' samples were dried at 70°C, there was little recovery in the ILSS for composites with 0% fibre surface treatment (51 MPa). For specimens with 10% fibre surface treatment the ILSS was fully recovered. For specimens with fibre surface treatments 25% and 100%, the ILSS was greater than for the 'as-received' specimens but the failures were very brittle.

As these dried specimens were exposed to 70°C and 95% RH again the value of the ILSS for specimens with no fibre surface treatment was similar to that obtained after the initial ageing (47 MPa), whereas specimens with 10% and 25% fibre surface treatments (batch 1) had strengths similar to those obtained after the first ageing. The batch 2 specimens with 25% and 100% fibre surface treatment had slightly higher values of interlaminar shear strengths after the second exposure to 70°C, 95% RH.

Comparing the results obtained after immersion of the specimens in boiling water and exposure to 50°C, 95% RH, the moisture absorbed by the boiled samples was greater and the loss in ILSS was also greater (Fig 13).

3.5 Microstructure

The fractured ILSS test pieces were examined to determine the failure mechanism.

The specimens with a fibre surface treatment of 2% showed no adhesion of the fibres to the resin (Fig 14). When these specimens were boiled for 1 week, the resin plasticised. This was indicated by the 'fluting' structure of the resin (Fig 15). Longitudinal cracks exist between the fibre and the matrix. As the 'wet' specimens were redried, the cracks remained but the plasticization of the resin was reversed although the resin structure looked different (Fig 16) to that of the 'as-received' specimens.

Fig 17 shows the fracture surface of an 'as-received' composite with 10% fibre surface treatment. The adhesion between the fibre and the matrix was very varied and may explain the large scatter observed in the moisture absorption and mechanical properties.

The specimens with 25% fibre surface treatment showed some fibres with no resin adhesion but the majority of the fibres showed good adhesion to the resin (Fig 18). On immersion in boiling water, the fibre-matrix bond was weakened and bare fibres could be seen on the fracture surfaces (Fig 19). On redrying the boiled samples, some of the adhesion was recovered but the fibres remained bare after fracture and longitudinal cracks between the fibres and the matrix were observed (Fig 20). The effect of exposing the composite with 25% fibre surface treatment to 50°C, 95% RH was not as severe. The resin plasticized and some of the strength of the fibre-resin interface bond was maintained.

In general, the immersion of specimens in boiling water caused failures at the fibre-resin interface leaving the fibres completely free of resin at the fracture surfaces, whereas the ageing at 50°C, 95%RH caused a less complete interface failure

resulting in microcracks between the fibres and the matrix. At the lower levels of fibre surface treatment, the poor adhesion of the resin allowed more deformation in the layers of the resin near the interface (*eg* Fig 15).

4 DISCUSSION

The fibre surface treatment of a carbon fibre composite determines the fibre-matrix bond strength; bond strength increases with fibre surface treatment[7]. The interlaminar shear test (ILSS) has been evaluated previously to monitor the fibre matrix interface properties[4]. In this work, as the fibre surface treatment was increased from 0% to 10% a marked increase in ILSS was observed. There was not much further increase in ILSS as the fibre surface treatment was increased from 10% to 100%. The compression strength of unidirectional composites[3] and the notch sensitivity of multidirectional laminates[2] show a similar trend. This implies that a 10% fibre surface treatment gives sufficient adhesion for adequate stress transfer between the matrix and the fibres.

The 10% surface treatment may also represent the critical case between a strong bond, in which the shear strength of the bond is greater than the shear strength of the resin, and a weak fibre matrix interface bond, where the bond shear strength is less than the shear strength of the resin. Hence for every resin matrix and its fibres, this critical fibre surface treatment may be different.

The effect of moisture is to reduce the shear properties of the CFRP composite by (a) weakening the fibre-matrix interface bond; (b) plasticizing the matrix and (c) weakening the matrix by creating microcracks in the resin caused by swelling stresses and moisture gradients.

Previous work on composites with standard (100%) surface treated fibres showed a decrease in ILSS with an increase in moisture content regardless of the mode of exposure to hot-wet environments[4]. Physical differences in the microstructure were however observed. In the present work an effect due to the method of exposure was observed, especially when the composite was subjected to more than one exposure, *ie* due to hygro-thermal cycling. Conflicting evidence for the reversibility of the effects of hygro-thermal cycling are quoted in the literature: Browning[8] claimed that it did not matter if the weight gain of a composite was due to immersion in water or exposure to a hot-humid environment and that the tensile, compressive and shear performances were fully reversible on the removal of water. Kaelble and Dynes[9] however found that the ILSS and work of fracture of composites was irreversible and associated with permanent changes in strength. Shen and Springer[10] explained the reversibility using Fickians diffusion theory. Other work[11] suggests a time-dependent microcracking in the resin and irreversibility as a function of the time. These effects are discussed below and a tentative explanation is given for this behaviour.

The results obtained can be divided into two groups: (i) specimens with fibre surface treatments below 5% and (ii) those with surface treatments in the range 5-100%.

For specimens with fibre surface treatments less than 5%, the moisture absorption, on immersion in boiling water was approximately twice as much as for the composites with

higher fibre surface treatments. Considering the fibre volume fraction to be 64% and assuming that the moisture is absorbed only in the resin, the composites with the higher fibre surface treatments absorbed 5.5% water in the resin, which is about average for an epoxy resin. The resin in the composite with the lower fibre surface treatments would have the equivalent of about 10% by weight moisture. This is excessive for any resin. This excess moisture is probably absorbed at the matrix-fibre interface. This would tend to break the bond between the fibre and the matrix and hence reduce the interlaminar shear strength as shown by the results. The swelling in these specimens was also large, especially in the thickness (~3.5%). This implies that more moisture is absorbed through the thickness of the specimens rather than the length or width. This moisture is probably absorbed into the cracks parallel to the surface of the specimen where the constraint due to the fibres is at a minimum. Also resin rich interply zones occur througn the thickness of the specimens and therefore more moisture can be absorbed.

The absorption of moisture, when the composites were exposed to 70°C and 95% RH, was much less (1.5 to 2.0%) than that obtained for composites immersed in boiling water especially for the lower fibre surface treated composites. The swelling was less and the decrease in the ILSS not as great as for the boiled samples, implying that the fibre-matrix interface was not as badly degraded as that of the boiled samples. Scanning electron fractographs showed more extensive damage (microcracking) in the boiled samples and this was irreversible. Some adhesion was recoverable for the samples exposed to a hot-humid environment. This again indicates the severity of the boiling water environment on the carbon fibre epoxy resin composite.

The swelling of the composite during moisture absorption and the contraction during the drying at 70°C, to a volume smaller than as-moulded, can only be explained in terms of thermodynamic molecular non-equilibrium in the material. This gives rise to free volume which when held at a temperature for a certain time relaxes and tends towards an equilibrium state. This reduces the free volume and also alters the behaviour of the material. This phenomenon has been observed by various authors for polymers[12] and specifically for epoxies[13] and is called the 'physical ageing' of a material. A summary of the results obtained here is given below in order to correlate these results with the theory.

When the 'wet' samples were dried in a vacuum oven at 70°C, all the composites retained a similar amount (0.5%) of moisture regardless of their initial exposure. This implies that this amount of moisture may be bound chemically in the resin and that a higher temperature would be required to dissociate it from the resin. The specimens that had been boiled initially, retained some of their swelling as they were dried but the specimens that had been exposed to 70°C and 95% RH contracted to give dimensional values less than those of the original (as-moulded) specimens. The ILSS values were not fully recovered for the boiled and dried samples. ILSS values were higher for the specimens dried after exposure to 70°C and 95% RH. It therefore seems that the interface bond and the matrix were altered for specimens immersed in boiling water.

According to the free volume theory, as a polymer is cooled from a high temperature, it is in a non-equilibrium state because the polymer molecules cannot move into an equilibrium state quickly enough as the quenching takes place. The resin therefore

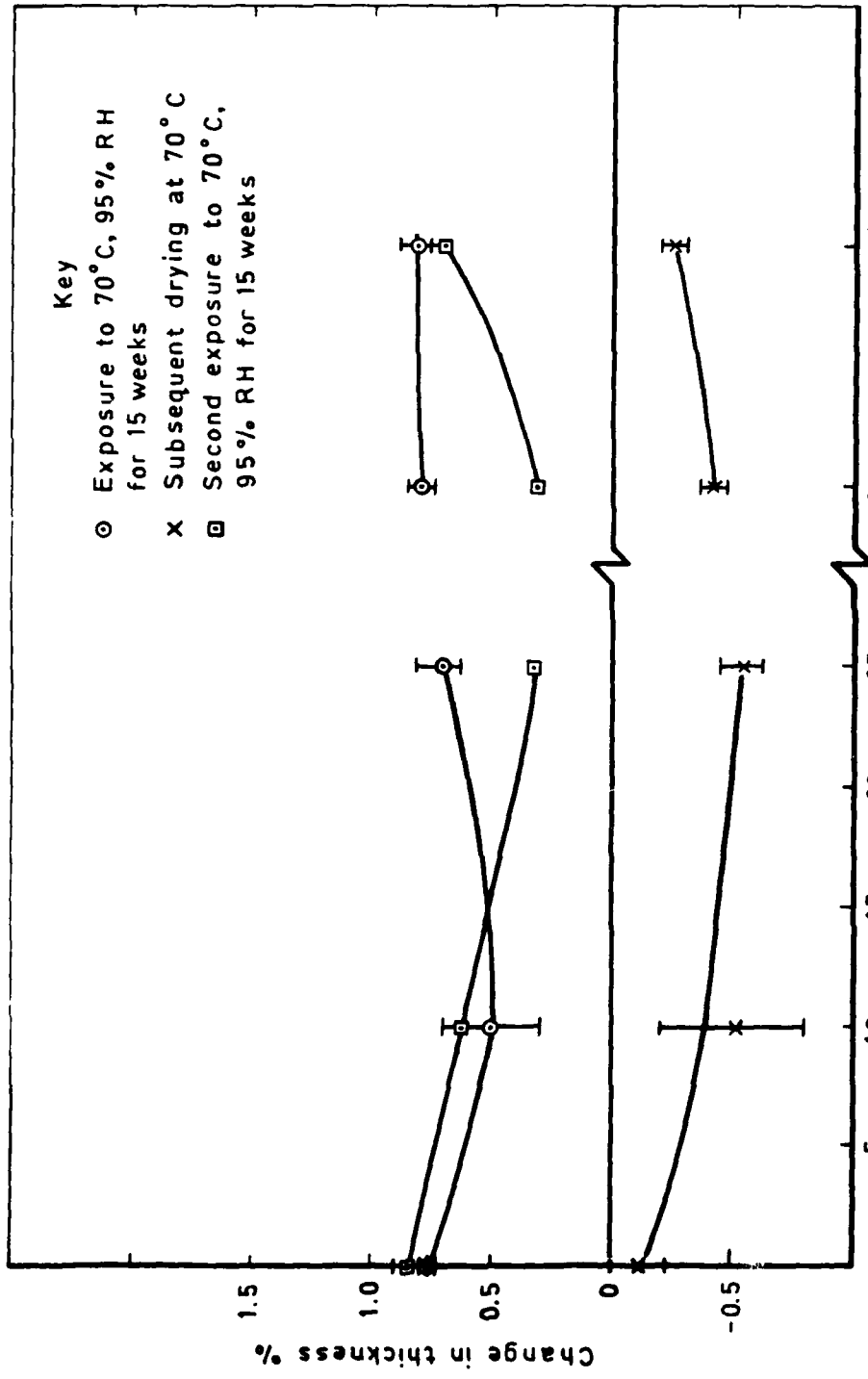

Fig 9 Change in thickness of unidirectional CFRP laminates with different levels of fibre surface treatment during hygrothermal cycling at 70°C, 95% RH

Fig 8

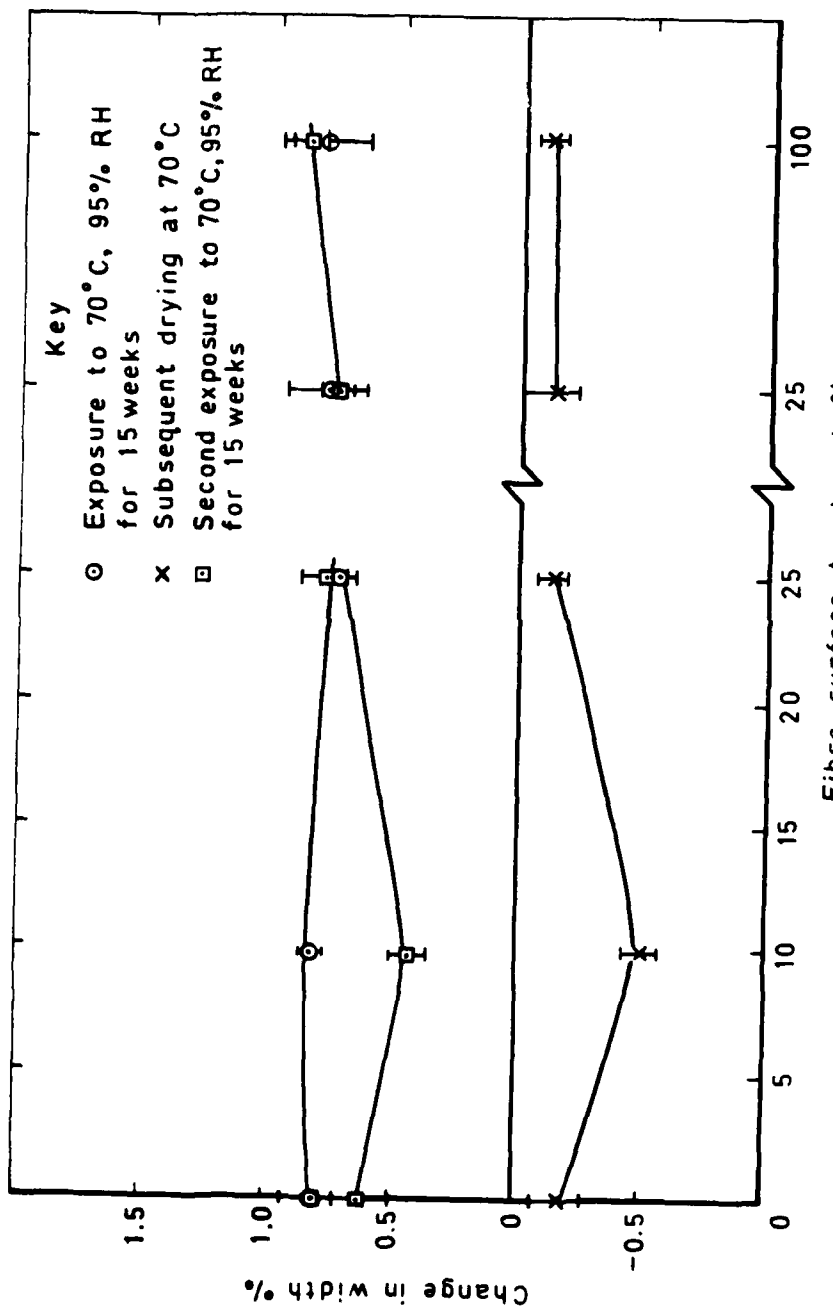

Fig 8 Change in width of unidirectional CFRP laminates with different levels of fibre surface treatment during hygrothermal cycling at 70°C, 95% RH

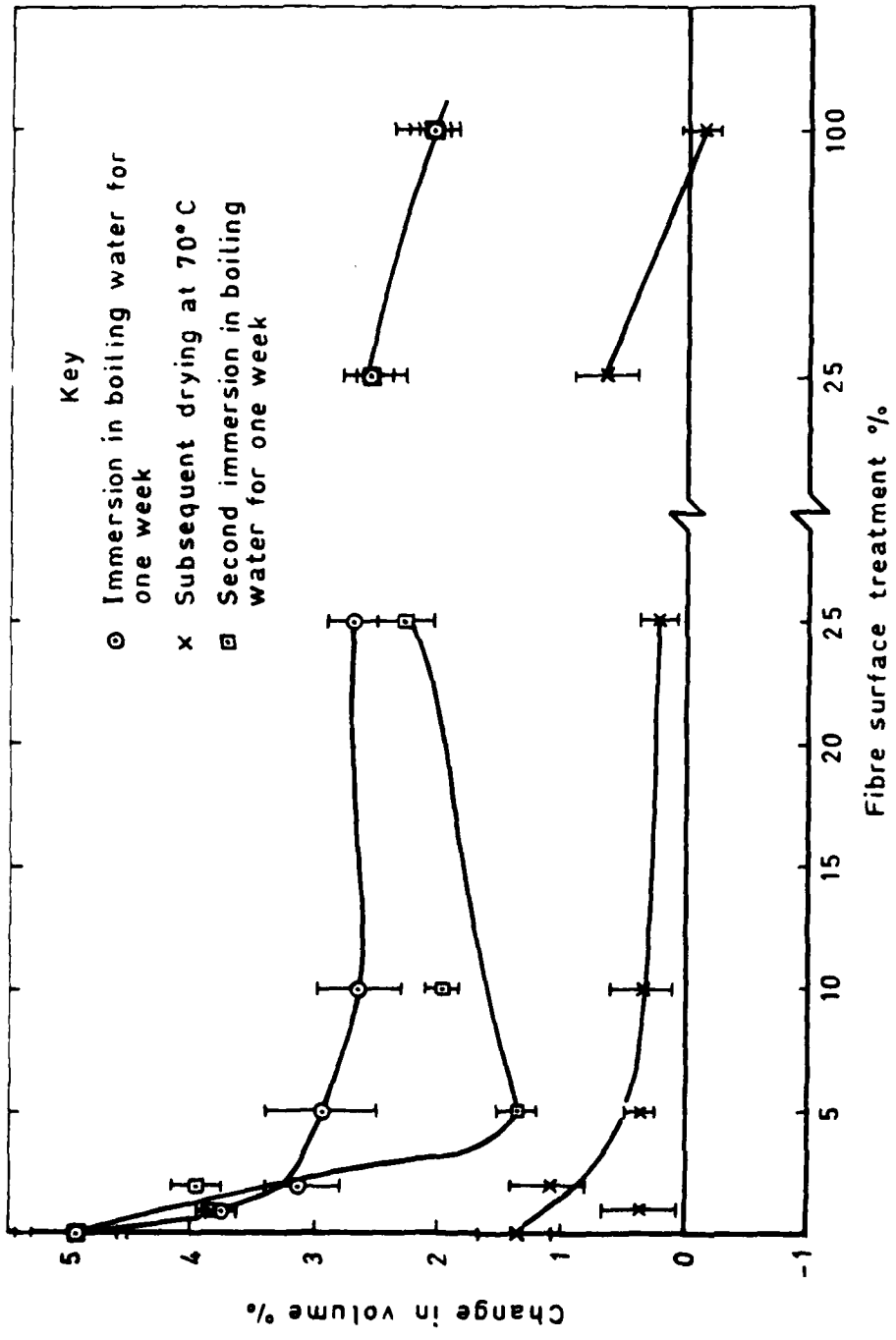

Fig 7 Change in volume of unidirectional CFRP laminates with different levels of surface treatment during hygrothermal cycling in boiling water

Fig 6

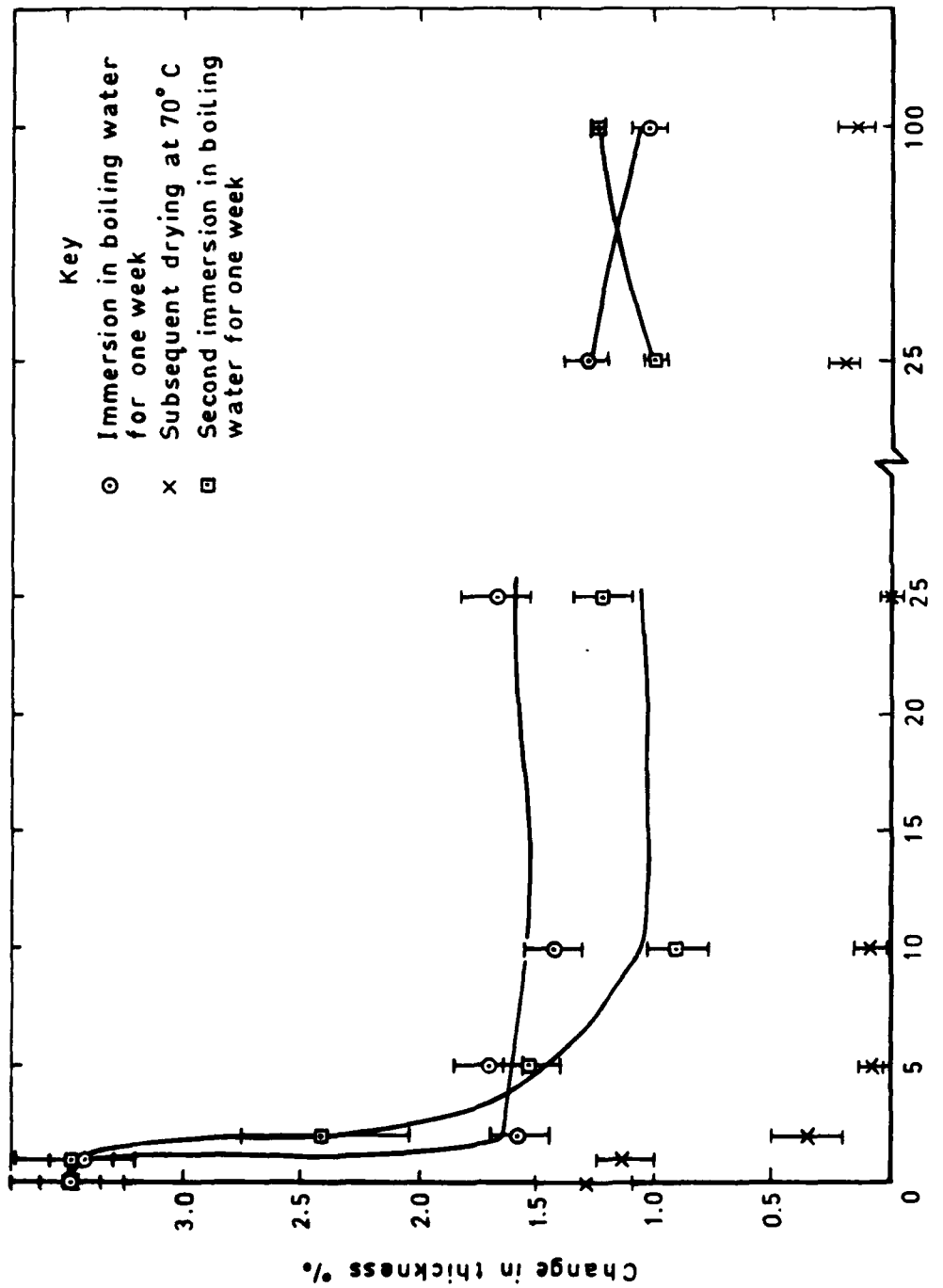

Fig 6 Change in thickness of unidirectional CFRP laminates with different levels of fibre surface treatment when hygrothermally cycled in boiling water

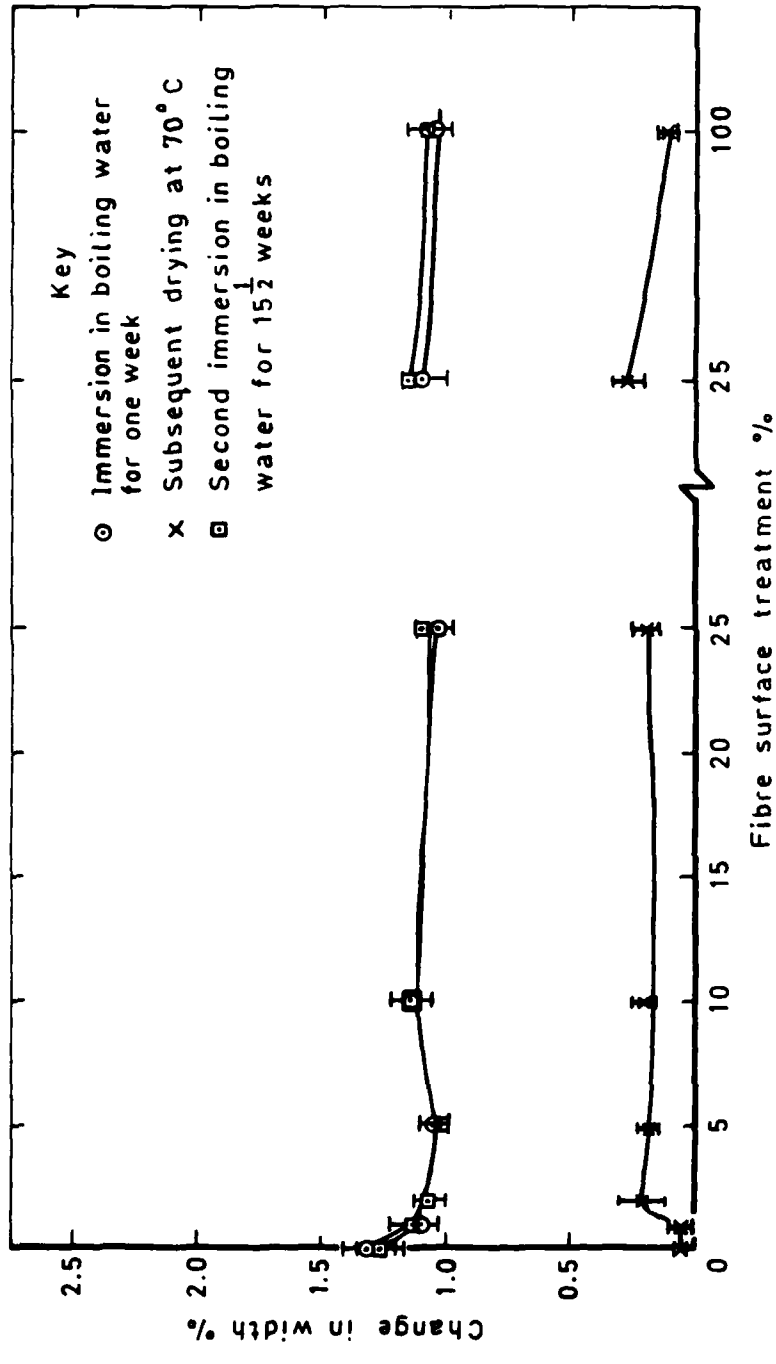

Fig 5 Change in width of unidirectional CFRP laminates with different levels of fibre surface treatment when hygrothermally cycled in boiling water

Fig 4

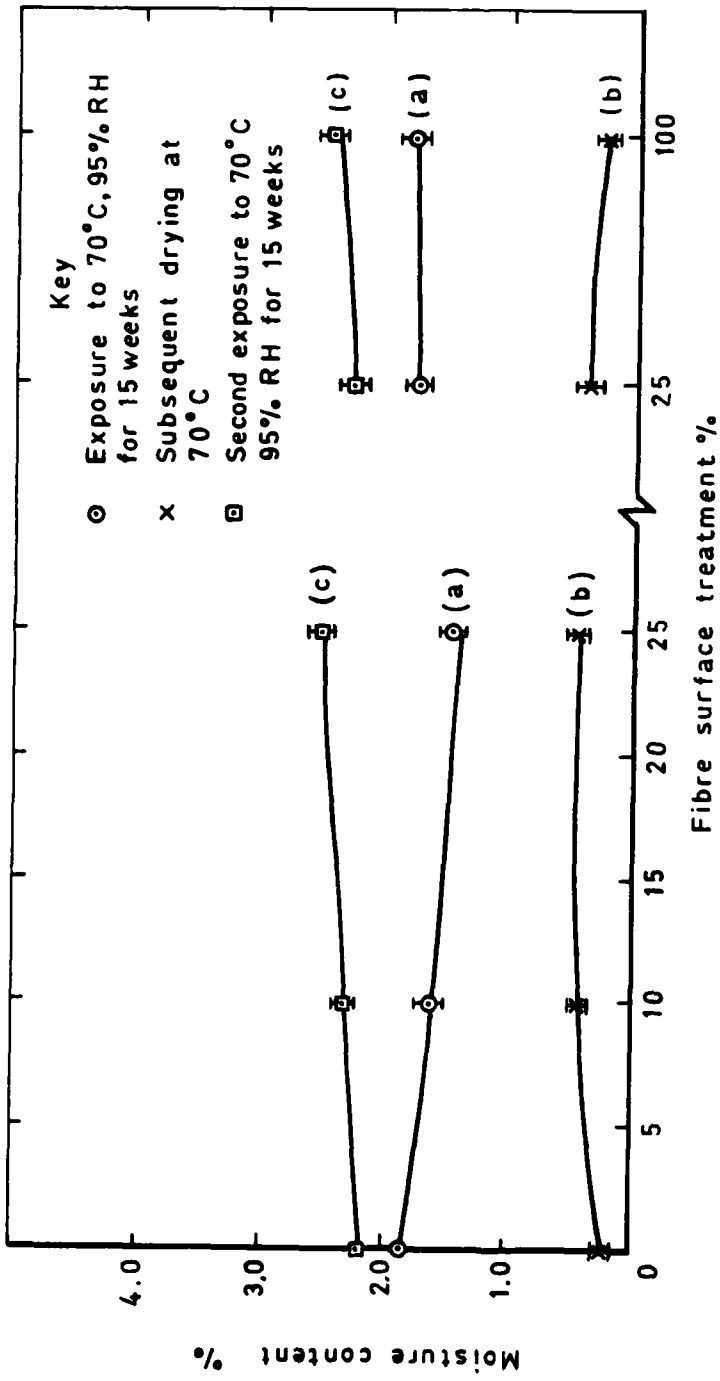

Fig 4 Moisture contents of unidirectional CFRP laminates with different levels of surface treatment when hygrothermally cycled at 70°C, 95% RH

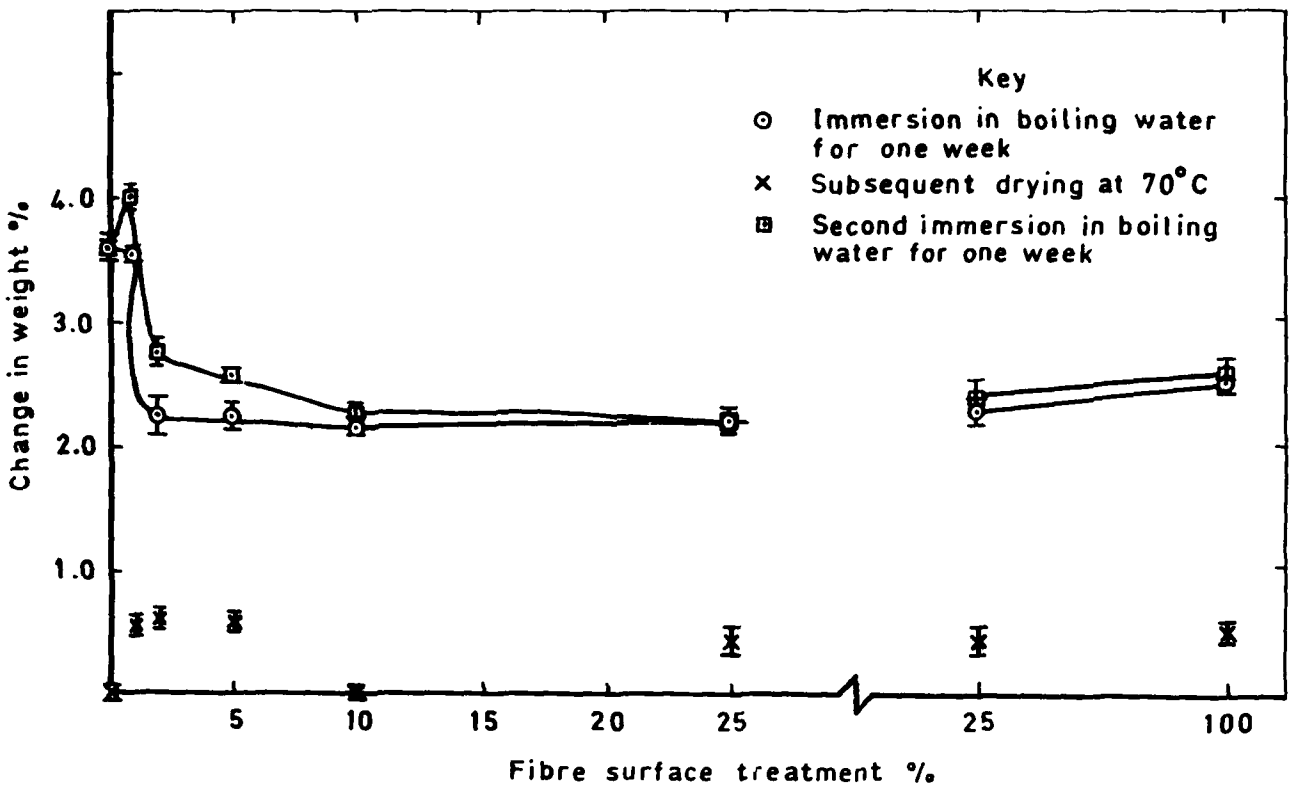

Fig 3 **Moisture contents of unidirectional CFRP laminates with different levels of fibre surface treatment during the hygrothermal cycling in boiled water**

Fig 3

Fig 2

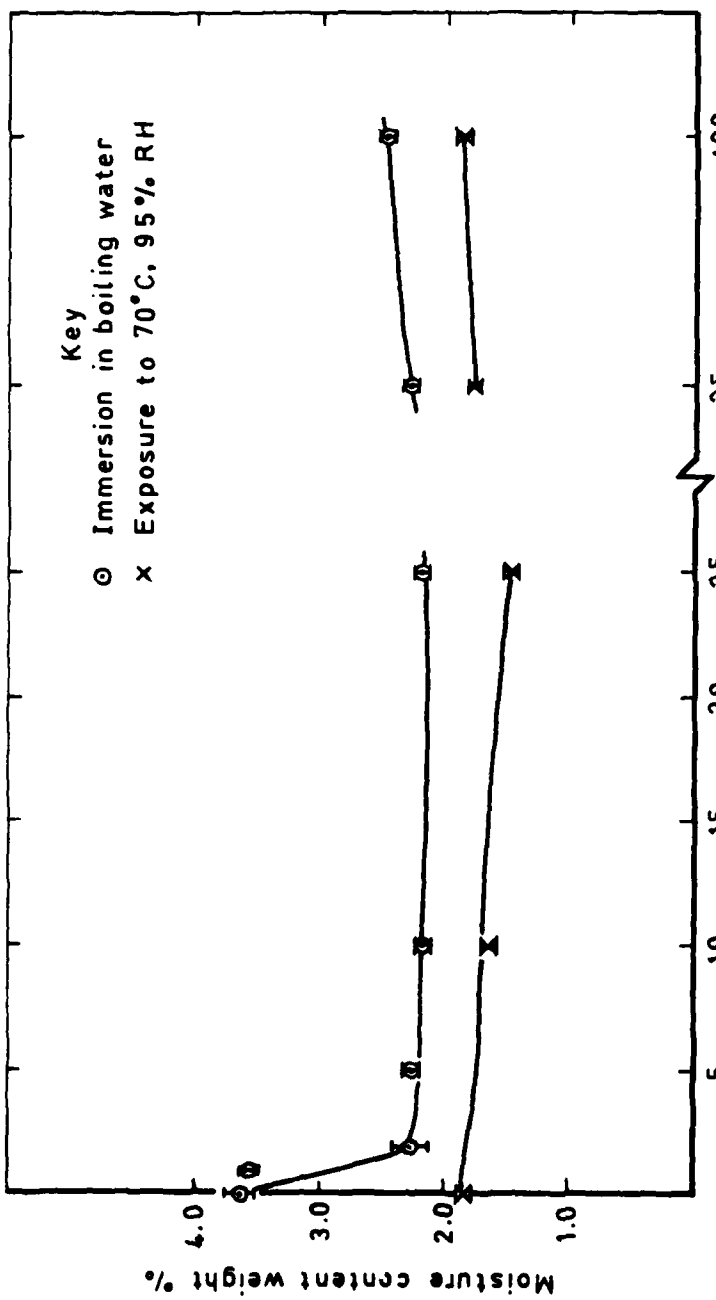

Fig 2 Moisture absorption in unidirectional CFRP laminates with different levels of fibre surface treatment after exposure to hot-wet environments

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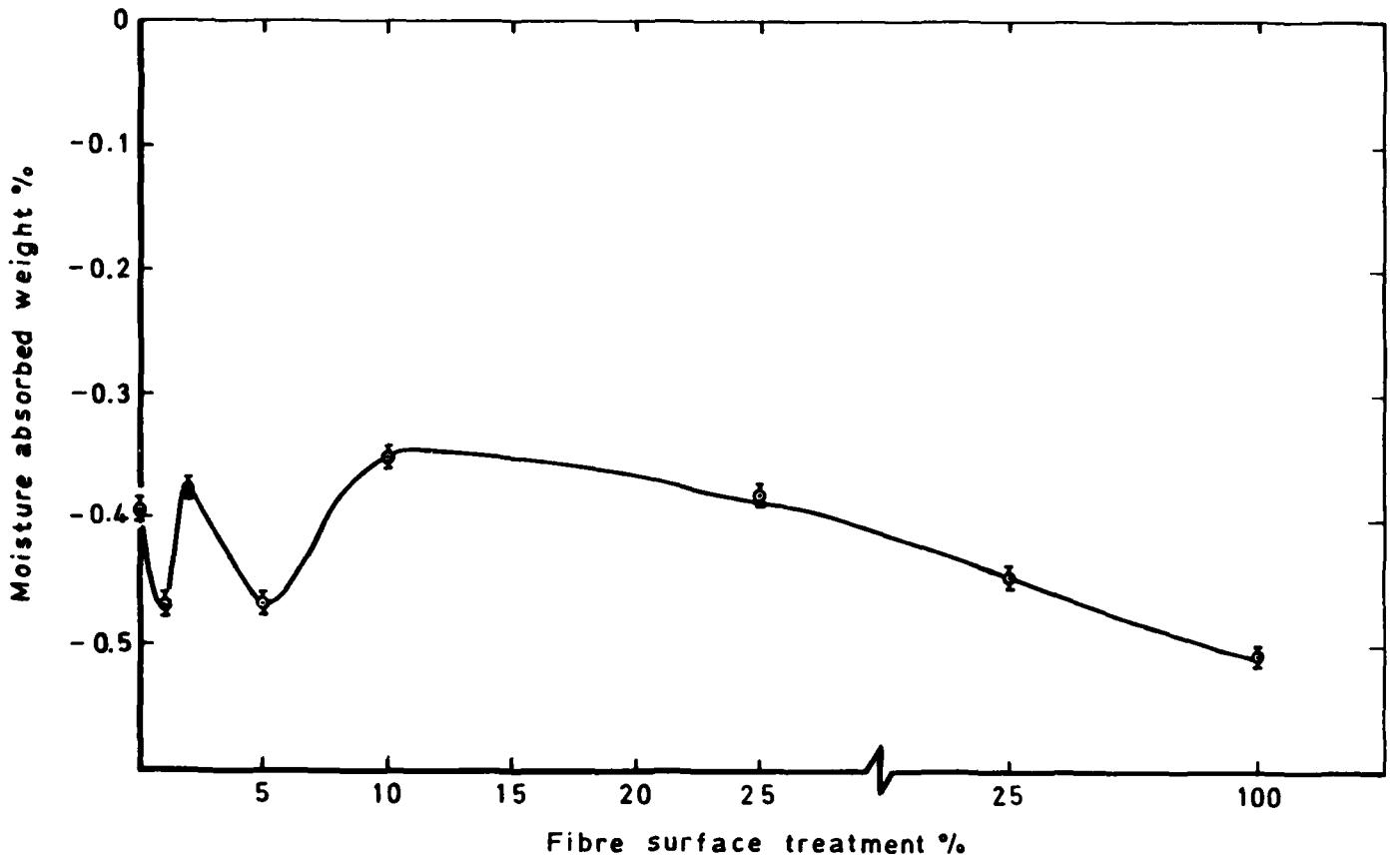

Fig 1 Weight loss when as-received unidirectional CFRP laminates with different levels of fibre surface treatments were dried at 70°C in a vacuum oven

Fig 1

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No.	Author	Title, etc
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Table 1

CHANGE IN LENGTH OF A UNIDIRECTIONAL CFRP LAMINATE WITH VARYING FIBRE SURFACE TREATMENT HYGROTHERMALLY CYCLED IN BOILING WATER

Fibre surface treatment (%)	Increase in length after immersion in boiling water (%)	Decrease in length after drying at 70°C (%)	Increase in length after a second immersion in boiling water (%)
Batch 1			
0	0.003	0.003	0.002
1	0.003	0.003	0.001
2	0.002	0.002	0.002
5	0.002	0.002	0.001
10	0.003	0.003	0.003
25	0.003	0.002	0.002
Batch 2			
25	0.002	0.001	0.005
100	0.002	0.002	0.004

Table 2

CHANGE IN LENGTH OF A UNIDIRECTIONAL CFRP LAMINATE WITH VARYING FIBRE SURFACE TREATMENT HYGROTHERMALLY CYCLE AT 70°C AND 95% RH

Fibre surface treatment (%)	Increase in length ($\delta L/L$) on ageing at 70°C, 95% RH (%)	Decrease in length on drying at 70°C (%)	Increase in length on re-ageing at 70°C, 95% RH (%)
Batch 1			
0	0.007	0.008	0.003
10	0.004	0.005	0.003
25	0.007	0.008	0.003
Batch 2			
25	0.001	0.003	0.008
100	0.002	0.003	0.003

In this study, the effect of the residual curing stresses has not been considered. Relaxation of these stresses due to moisture absorption would enhance the swelling and increase the free volume in the matrix.

Summarising the points discussed, the ILSS of CFRP composites is dependent on the strength of the fibre-resin interface bond and the stiffness of the resin itself. The latter is affected by the amount of moisture present in the resin which in turn depends on the fibre surface treatment and the mode of exposure of the composite to a hot-wet environment. Plasticization and molecular re-arrangement due to a change in 'free volume' state also alter the resin properties. This process is time-dependent and therefore has to be considered carefully when correlating accelerated ageing tests done on materials soon after curing with those in real-life applications, and when predicting long-term properties and/or behaviour of the materials in service.

5 CONCLUSIONS

(1) For the eight carbon fibre epoxy resin composites with varying amounts of fibre surface treatments between 0% and 100%, the ILSS increased by about 33% as the carbon fibre surface treatment was increased from 0% to 10%, with no further increase up to 100% fibre surface treatment.

(2) The effect of absorbed moisture was to reduce the ILSS of all the composites. The greatest reductions occurred for the specimens with fibre surface treatments below 10% and for specimens immersed in boiling water. This was due to the loss of the interface bond. Moisture absorption was also greater for specimens with the lower fibre surface treatments. The effect of exposure to 70^{o}C 95% RH was less severe than immersion in boiling water. Thus, the mode of exposure was considerdd to be of importance for composites which do not have a good fibre-matrix interface bond.

(3) The boiled specimens with higher fibre surface treatments (greater than 10%) recovered 90% of their ILSS when dried at 70^{o}C in a vacuum oven. The specimens which were initially exposed to 70^{o}C and 95% RH and then dried at 70^{o}C had higher ILSS than their initial as-received values. This was attributed to the phenomenon of 'physical ageing' in which the matrix tended towards its low temperature molecular equilibrium from a state in which the higher free volume associated with the higher cure temperatures had been 'frozen in' by the rapid cooling from the moulding temperature.

possesses molecules that are 'frozen' and excess free volume is trapped within the whole structure. The molecular equilibrium would be achieved in time as the molecule moved in the epoxy resin at a temperature T below its Tg . Volume recovery would continue as the material 'aged'.

Kong *et al*[14] observed that this type of ageing affected the sorption level of neat epoxy resins due to a decrease in free volume of the resin. Further work[14] showed enthalphy relaxation peaks during the ageing at a temperature of 80°C. The energy released was equivalent to the activation energy required to break hydrogen bonds (2-3 kcal/mol). He therefore suggested that during ageing, hydrogen bonds were being broken and then reformed to reduce the available free volume in the resin. He showed that thermal expansion was a function of the ageing time and that the aged specimens always had a smaller volume than the 'as-quenched' specimens. However if the ageing temperature was below the Tg of the specimen, then the thermal expansion decreased with the ageing temperature, but if the ageing temperature was above the Tg of the specimen, then the thermal expansion increased with the ageing temperature. Also, the expansion was a function of the re-ageing time. For the epoxy resin/graphite fibre systems studied by Kong[15] the toughness and VTS decreased with ageing.

Absorbed moisture in CFRP composites (tested here) could affect the properties in two ways:

(i) the absorbed moisture would reduce the Tg of the epoxy resin.

(ii) The absorbed moisture could affect the molecular arrangement in the resin by making the OH^- and H^+ ions available to the system.

In the BSL 914/XA system, the effect of the absorbed moisture (1.5% in composite and equivalent of 4% in the resin) after exposure to 70°C, 95% RH would be to reduce the Tg of the resin by about 80°C to about 120-140°C. The drying temperature of 70°C is still much below the Tg of the 'wet' composite. Hence, as the drying occurs, 'ageing' of the material takes place below the Tg and hence a decrease in the free volume would be expected. In the case of the specimens initially immersed in boiling water, the moisture absorbed in the composite was higher (of the order of 2.1%, equivalent of 5.5% in resin) and thus the decrease in the Tg of the resin would be of the order of 100-120°C to a value of between 100°C and 80°C. Thus, the drying temperature of 70°C, is near the Tg of the wet composite. Hence, an increase in the free volume would be expected and a retention of the swelling in the composite.

On re-exposing the dried samples in their original hot-wet conditions, the specimens immersed in boiling water re-absorbed moisture, the amount being similar to that absorbed during the initial immersion, and the ILSS had similar values. This implies that the damage was mainly physical, and irreversible and was completed during the first cycle. This agreed with suggestions made by Kaelble and Dynes[9]. The specimens that were exposed to 70°C, 95% RH absorbed more moisture during the second exposure and the ILSS values were lower than those obtained after the initial ageing. This indicates the difference in the chemistry of the resin and the physical nature of the matrix due to the swelling which was slightly greater during the second exposure.

Fig 10

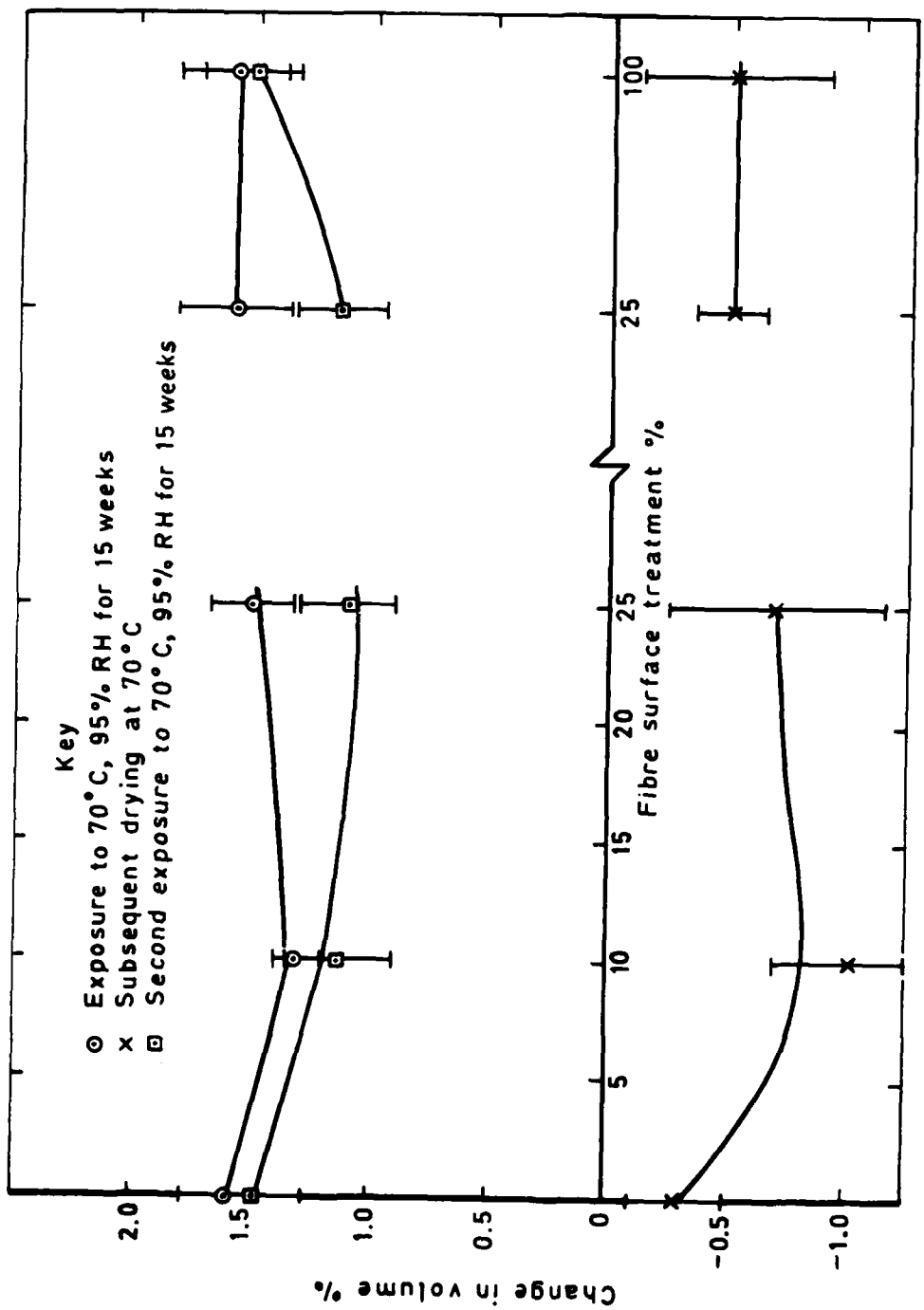

Fig 10 Change in volume of unidirectional CFRP laminates with different levels of fibre surface treatment during the hygrothermal cycling at 70°C, 95% RH

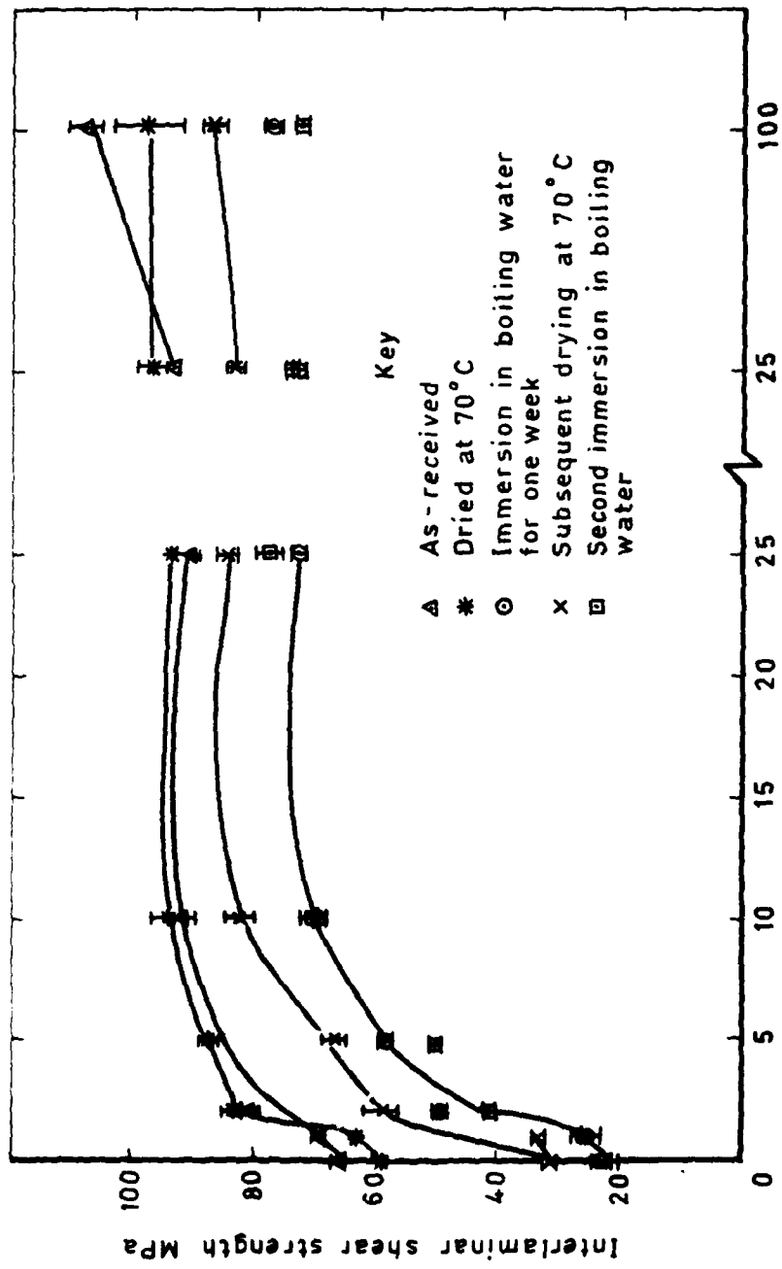

Fig 11 Variation of interlaminar shear strength with the change in fibre surface treatment of BSL 914/XA hygrothermally cycled in boiling water

Fig 12

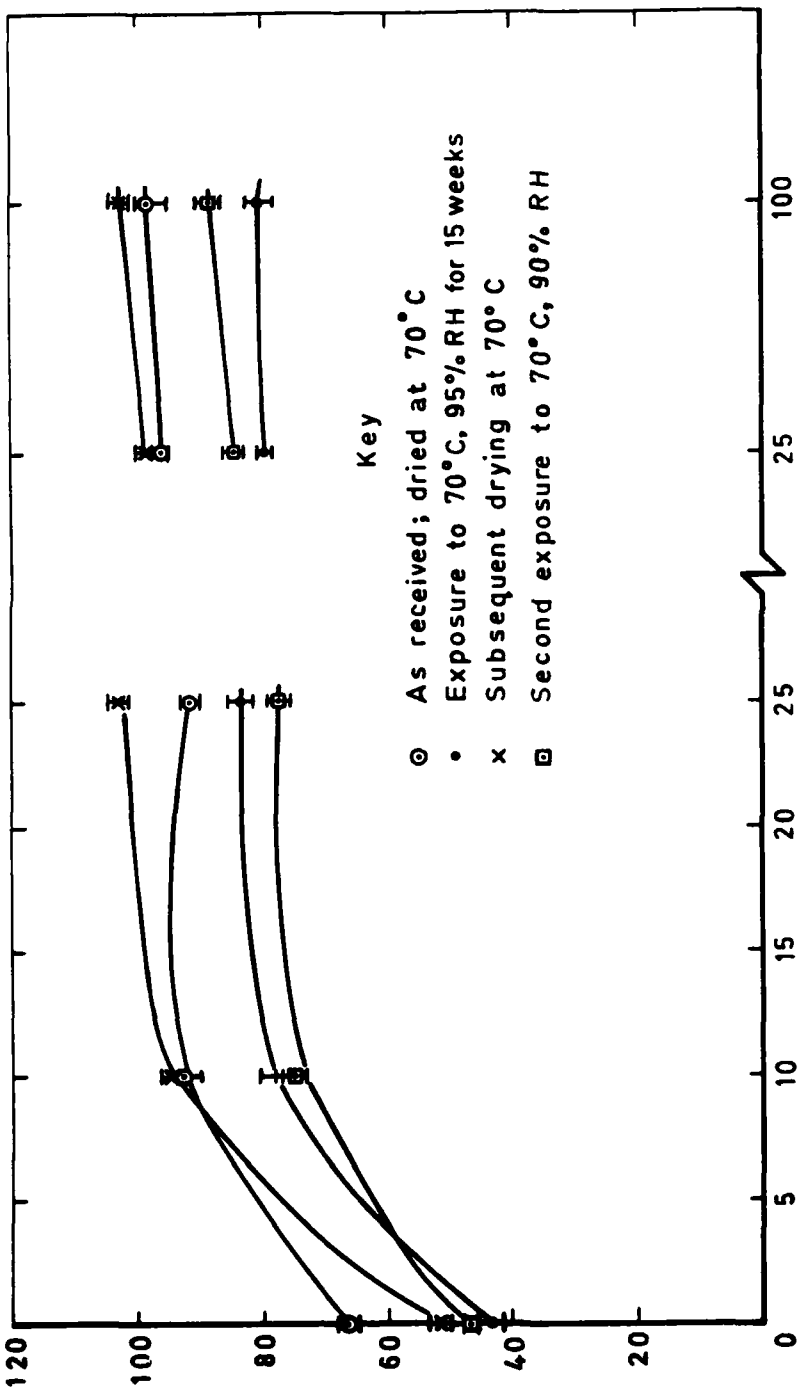

Fig 12 Variation of interlaminar shear strength with the change in fibre surface treatment of BSL 914/XA hygrothermally cycled at 70°C, 95% RH

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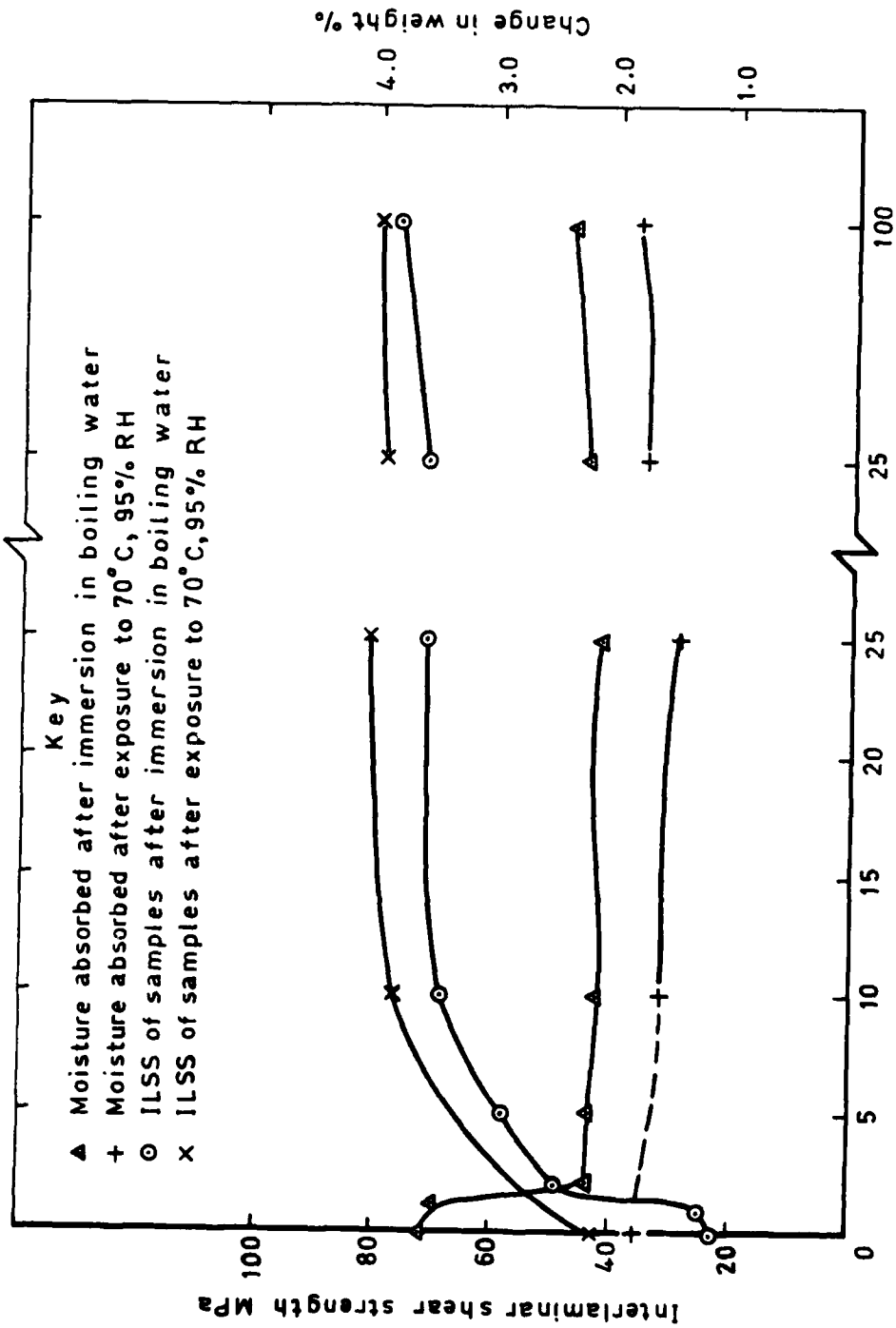

Fig 13 Effect of the mode of exposure on the properties of unidirectional CFRP laminates

Figs 14&15

Fig 14 Shear surface of 'as-received' sample of CFRP with 2% fibre surface treatment (x1200)

Fig 15 Shear surface of CFRP with 2% fibre surface treatment immersed in boiling water for one week (x2000)

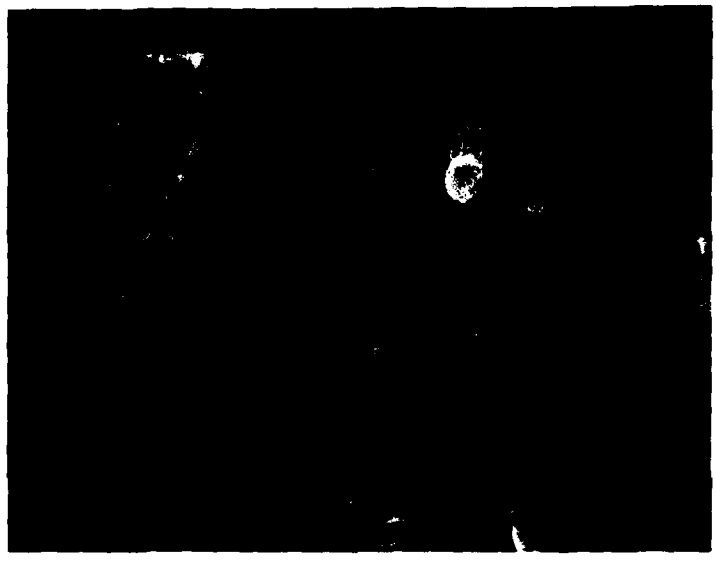

Fig 16 Shear surface of CFRP with 2% fibre surface treatment dried after immersion in boiling water (x6600)

Fig 17 Shear surface of 'as-received' CFRP with 10% fibre surface treatment (x1000)

Figs 18&19

Fig 18 Shear surface of 'as-received' CFRP with 25% fibre surface treatment (x2200)

Fig 19 Shear surface of CFRP with 25% fibre surface treatment immersed in boiling water for 1 week (x1000)

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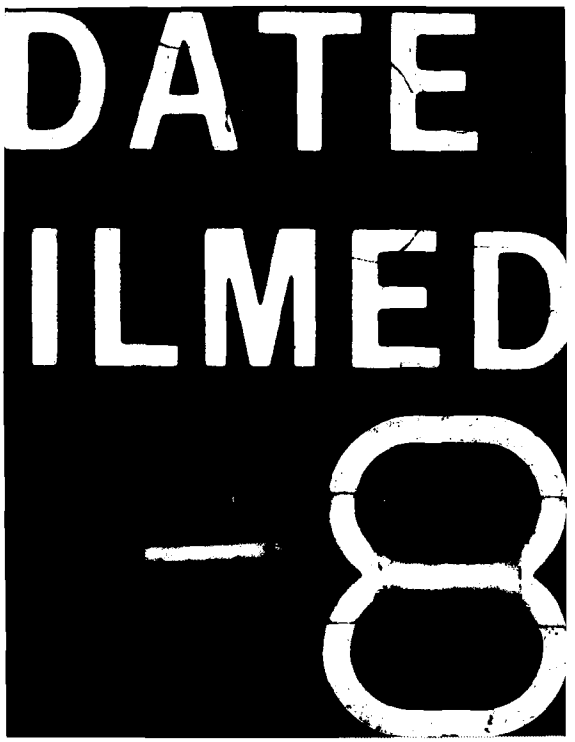
Fig 20 Shear surface of CFRP with 25% fibre surface treatment dried after immersion in boiling water (x2000)

Fig 21 Shear surface of CFRP with 25% fibre surface treatment after exposure to 50°C and 95% RH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